

# Non-adiabatic coupling and adiabatic population transfer in quantum molecular systems

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We show that a counter-intuitive pulse sequence leads to adiabatic passage between the vibrational levels of three harmonic potentials through parallel dark states in adiabatic approximation. However, the adiabatic assumptions break down for very intense pulses and non-adiabatic couplings result in the population transfer by light-induced potential shaping.

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Population transfer by shaping light induced potentials (LIP) is a very robust scheme to transfer vibrational population between different electronic potentials in diatomic molecules [1, 2, 3, 4, 5, 6]. One of the main advantages of the scheme is that the vibrational quantum number is conserved during the overall process. Since the selectivity of the transfer is guaranteed by a symmetry rule, the method is not very sensitive to the exact position of the energy resonance, i.e. to the topological or energetic features of the potentials involved.

The simplest scenario of population transfer by shaping LIP can be described in terms of three electronic states (potential curves) sequentially coupled by two laser pulses, and the vibrational population is driven by two photon off resonant absorption. Although there are several possible scenarios for selective population transfer [1, 7], the first scheme proposed, called APLIP, involves a sequence of two very strong (TW/cm<sup>2</sup>) picosecond pulses applied in counter-intuitive order [5]. The pulse that couples the intermediate electronic state with the final excited electronic state must precede the pulse that couples the ground electronic state with the intermediate one. Then the system dynamics follows a characteristic pattern in the vibrational basis representation, which is illustrated in Fig. 1 for a test system of three harmonic oscillators with the same force constant. (More details about the model are presented below.) According to Fig. 1(a), the overall population on the ground electronic state is rapidly transferred to the final electronic state, while very few population is temporally excited to the intermediate electronic state. So, in principal it is possible to suppose there is a dark state consisting of the initial and final potentials, similar to the population transfer through the dark state of the three-level system [8]. Looking into the vibrational populations in detail, it can be seen that the passage is mediated by substantial excitation of high energy vibrational levels in both initial and final potentials, Fig. 1(b).

The scenario previously considered is very similar to the well known Stimulated Raman Adiabatic Passage (STIRAP) scheme [8]. In STIRAP there are three levels sequentially coupled by two fields working in counter-

intuitive order. This arrangement of pulses prepares the system initially in a dark state,  $|\Phi_0\rangle$ , which is an eigenstate of the Hamiltonian dressed by the field in the adiabatic approximation. The dark state correlates at late times with the final level  $|3\rangle$  and never overlaps with the intermediate level. The population is transferred from  $|1\rangle$  to  $|3\rangle$  in a completely similar way to the overall electronic populations of Fig. 1(a).

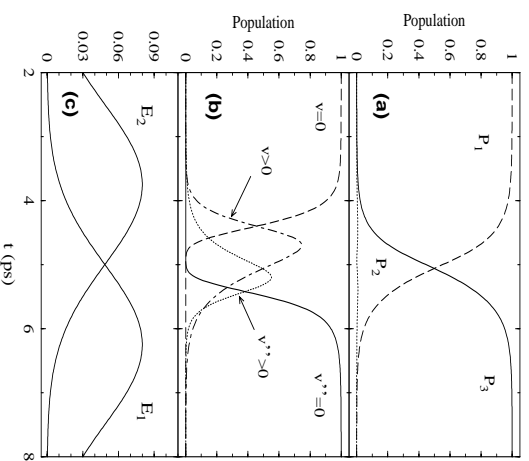


FIG. 1: Population dynamics in three symmetrically displaced harmonic oscillators model. (a) Solid line shows the total population of final state, dashed line shows the population of ground state, and dotted line is the population of intermediate state. (b) Population of vibrational levels, dashed line - zero vibrational level of ground state, dot-dashed line - population of the vibrational levels  $v > 0$  of ground state, solid line - population of zero vibrational level of final state, dotted line - population of the vibrational levels  $v'' > 0$  of the final state. (c) Shape of the laser pulses.

Normally, the STIRAP scheme involves nanosecond (or longer) pulses with intensities in the GW/cm<sup>2</sup> (or less). Therefore it is natural to ask if APLIP is a short time, strong field version of STIRAP (and applied to electronic states instead of vibrational or atomic levels). Indeed the requirement of stronger laser fields can be understood un-

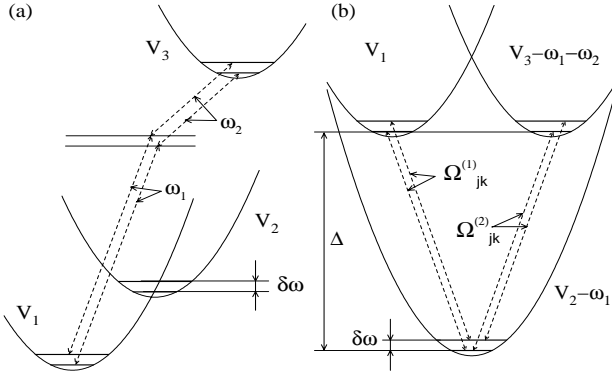


FIG. 2: (a). Scheme of three symmetrically displaced harmonic oscillators truncated to give two coupled 3-level ladder systems. (b). Dressed potentials,  $U_1 = V_1$ ,  $U_2 = V_2 - \omega_1$ , and  $U_3 = V_3 - \omega_1 - \omega_2$ .

der the general assumptions of STIRAP. Since the adiabaticity condition in STIRAP is usually expressed by the pulse area relation,  $\Omega\tau \gg 1$ , where  $\Omega$  is the effective Rabi frequency of the pulses and  $\tau$  their time widths, any reduction in the pulse width must imply a corresponding increase in the pulse amplitude. Nevertheless, in this note we show that the population transfer in APLIP can not be reduced to the generalized description of STIRAP in multi-level system. In order to do so we show that the natural extension of STIRAP to the three potential curves scenario in the strong field limit predicts a different dynamical evolution than the one shown in Fig. 1.

Let us consider in detail the Hamiltonian of the system. The Hamiltonian for three electronic potentials ( $V_i(x)$ ,  $i = 1, 2, 3$ ) coupled by two laser fields ( $E_1(t)$  and  $E_2(t)$ ) in the Born Oppenheimer and rotating wave approximation (RWA) reads

$$H^{RWA} = \begin{pmatrix} T + U_1(x) & -\frac{1}{2}\mu_{12}(x)E_1(t) & 0 \\ -\frac{1}{2}\mu_{12}(x)E_1(t) & T + U_2(x) & -\frac{1}{2}\mu_{23}(x)E_2(t) \\ 0 & -\frac{1}{2}\mu_{23}(x)E_2(t) & T + U_3(x) \end{pmatrix}, \quad (1)$$

where  $T$  is the kinetic energy operator and  $U_i(x)$  are the diabatic dressed potentials ( $U_1(x) = V_1(x)$ ,  $U_2(x) = V_2(x) - \omega_1$ ,  $U_3(x) = V_3(x) - \omega_1 - \omega_2$ ,  $\omega_i$  being the carrier frequencies of the lasers),  $\mu_{12}(x)$  and  $\mu_{23}(x)$  are the dipole moments (atomic units are used throughout). In this representation the global wave function of the system is expanded in terms of electronic wave functions,  $\{\Xi_i(q; x)\}$ , and vibrational wave packets,  $\{\psi_i(x, t)\}$ , where  $q$  is an index representing the collective electron coordinates and  $x$  is the vibrational coordinate.

After expanding the vibrational wave packet in the set of eigenfunctions of the vibrational Hamiltonian for each potential,

$$\psi_\alpha(x, t) = \sum_j d_j^{(\alpha)}(t) \phi_j^{(\alpha)}(x), \quad (2)$$

where  $\phi_j^{(\alpha)}(x)$  is the  $j$ 'th vibrational level in the electronic state  $\alpha$  (in the following we use Greek letters to designate electronic states and Roman letters to designate vibrational levels), we arrive at the following time dependent Schrödinger equation (TDSE):

$$\begin{cases} i\dot{d}_j^{(1)} = (\omega_j^{(1)} + \omega_1 + D_1^0 - D_2^0)d_j^{(1)} - \sum_k \frac{\Omega_{jk}^{(1)}}{2}d_k^{(2)} \\ i\dot{d}_j^{(2)} = -\sum_k \frac{\Omega_{jk}^{(1)}}{2}d_k^{(1)} + (\omega_j^{(2)} - D_2^0)d_j^{(2)} - \sum_k \frac{\Omega_{jk}^{(2)}}{2}d_k^{(3)} \\ i\dot{d}_j^{(3)} = -\sum_k \frac{\Omega_{jk}^{(2)}}{2}d_k^{(2)} + (\omega_j^{(3)} - \omega_2 + D_3^0 - D_2^0)d_j^{(3)}, \end{cases} \quad (3)$$

where  $\omega_j^{(\alpha)} + D_\alpha^0$  is the eigenvalue corresponding to the  $|\phi_j^{(\alpha)}\rangle$  eigenfunction,  $\Omega_{ij}^{(1)} = E_1(t)\langle\phi_i^{(1)}|\mu_1|\phi_j^{(2)}\rangle$  and  $\Omega_{ij}^{(2)} = E_2(t)\langle\phi_i^{(3)}|\mu_2|\phi_j^{(2)}\rangle$  are the Rabi frequencies, and  $D_\alpha^0$  are the potential zero energies.

In order to compare the dynamics of the general system with that of STIRAP, we establish a correspondence between the  $3 \times N$  equations of motion (Eq. (3)) and the equations for  $N$  3-level ladder systems, where both diabatic and adiabatic states are known, corresponding to that of the STIRAP Hamiltonian. In doing this connection we neglect all the contributions from the continuum wave functions in all the electronic states. To simplify the notation we use a model of three symmetrically displaced harmonic oscillators (Fig. 2) with the same force constant (SDHO model), so that the separation between the minima of the potentials is constant,  $r_0^{(3)} - r_0^{(2)} = r_0^{(2)} - r_0^{(1)} = R$ . We assume that the equilibrium configurations of the excited potentials are displaced to larger inter nuclei distances. Furthermore we consider only processes in two photon resonance. This allows us to define a constant energy splitting,  $\delta\omega = \omega_{n+1}^{(1)} - \omega_n^{(1)} = \omega_{n+1}^{(3)} - \omega_n^{(3)}$ , and a one photon detuning,  $\Delta = D_2^0 - \omega_0^{(1)} - \omega_1 = (\omega_2 + D_2^0) - \omega_0^{(3)} - D_3^0$ .

The TDSE is:

$$\begin{cases} id_j^{(1)} = (j\delta\omega - \Delta)d_j^{(1)} - \sum_k \frac{\Omega_{jk}^{(1)}}{2}d_k^{(2)} \\ id_j^{(2)} = -\sum_k \frac{\Omega_{jk}^{(1)}}{2}d_k^{(1)} + (j\delta\omega)d_j^{(2)} - \sum_k \frac{\Omega_{jk}^{(2)}}{2}d_k^{(3)} \\ id_j^{(3)} = -\sum_k \frac{\Omega_{jk}^{(2)}}{2}d_k^{(2)} + (j\delta\omega - \Delta)d_j^{(3)}. \end{cases} \quad (4)$$

Finally we invoke the Condon approximation. Therefore, the state to state Rabi frequencies can be expressed as  $\Omega_{ij}^{(1)} = p_{ij}^{12}\mu_1 E_1(t)$  and  $\Omega_{ij}^{(2)} = p_{ij}^{23}\mu_2 E_2(t)$ , where we have defined the geometric Franck-Condon parameters  $p_{ij}^{\alpha\beta} = \langle \phi_i^{(\alpha)} | \phi_j^{(\beta)} \rangle$ . This is the model used to obtain the results shown in Fig. 1, where we have chosen  $\delta\omega = 7 \cdot 10^{-4}$  a.u.,  $\Delta = 0.015$  a.u.,  $\mu_1 = \mu_2 = 1$ ,  $E_i(t) = E_0 S(t)$ , with  $E_0 = 0.08$  a.u. and  $S(t)$  being a Gaussian envelope function. Both pulses have the same envelope function, with width  $\sigma = 2.5$  ps and they are time delayed, so that the second pulse precedes in 2.5 ps the first pulse. To obtain the numerical results shown in Fig. 1 we have numerically integrated the TDSE based on a grid discretization of the Hamiltonian in Eq. (1) and not on the discrete basis representation of Eq. (4). Details of the numerical propagator are given in reference [2].

In order to go further in the comparison between the set of Eqs. (4) and those of STIRAP, we change the representation from the diabatic basis  $\{\phi_n^{(1)}, \phi_n^{(2)}, \phi_n^{(3)}\}$  to the

adiabatic basis of the 3-levels ladder system for each  $n$  sub-system,  $\{\Phi_+^{(n)}, \Phi_0^{(n)}, \Phi_-^{(n)}\}$ , using the block diagonal rotation matrix  $\hat{R} = \hat{R}_1 \dots \oplus \hat{R}_n \dots \oplus \hat{R}_N$  with

$$\hat{R}_n = \begin{pmatrix} \sin \varphi_n \sin \theta_n & \cos \theta_n & \cos \varphi_n \sin \theta_n \\ \cos \varphi_n & 0 & -\sin \varphi_n \\ \sin \varphi_n \cos \theta_n & -\sin \theta_n & \cos \varphi_n \cos \theta_n \end{pmatrix}, \quad (5)$$

where the angles are defined by  $\tan \theta_n = \Omega_{nn}^{(1)}/\Omega_{nn}^{(2)}$  and  $\tan(2\varphi_n) = 2 \left( \sqrt{(\Omega_{nn}^{(1)})^2 + (\Omega_{nn}^{(2)})^2} \right) / \Delta$ .

In the new representation, the dynamics of the system is followed by the amplitude coefficients  $\{a_+^{(n)}, a_0^{(n)}, a_-^{(n)}\}$ , which are delocalized and follow the electronic transitions between the potentials at different moments of time. The new basis is *quasi-adiabatic* since the transformation matrix  $\hat{R}$  diagonalizes only each  $3 \times 3$  sub-system matrices, while there remain couplings between different sub-systems.

To illustrate the nature of these couplings, we detail the analysis for a system of 6-levels obtained by truncating the expansion of the wave function (Eq. (2)) to only the first two vibrational levels. We consider these levels as belonging to two coupled 3-level ladder systems, whose Hamiltonian is

$$H = \begin{pmatrix} \hat{H}_{11} & \hat{H}_{12} \\ \hat{H}_{21} & \hat{H}_{22} \end{pmatrix} = -\frac{1}{2} \begin{pmatrix} 0 & \Omega_{11}^{(1)} & 0 & 0 & \Omega_{12}^{(1)} & 0 \\ \Omega_{11}^{(1)} & 2\Delta & \Omega_{11}^{(2)} & \Omega_{12}^{(1)} & 0 & \Omega_{12}^{(2)} \\ 0 & \Omega_{11}^{(2)} & 0 & 0 & \Omega_{12}^{(2)} & 0 \\ 0 & \Omega_{21}^{(1)} & 0 & -2\delta\omega & \Omega_{22}^{(1)} & 0 \\ \Omega_{21}^{(1)} & 0 & \Omega_{21}^{(2)} & \Omega_{22}^{(1)} & -2(\delta\omega - \Delta) & \Omega_{22}^{(2)} \\ 0 & \Omega_{21}^{(2)} & 0 & 0 & \Omega_{22}^{(2)} & -2\delta\omega \end{pmatrix}, \quad (6)$$

and we next change the representation using  $\hat{R} = \hat{R}_1 \oplus \hat{R}_2$  ( $\hat{R}_n$  is given by Eq. (5)). We obtain the quasi-adiabatic Hamiltonian

$$\begin{aligned} \hat{H}^{CD} &= \begin{pmatrix} \hat{R}_1^{-1} & 0 \\ 0 & \hat{R}_2^{-1} \end{pmatrix} \begin{pmatrix} \hat{H}_{11} & \hat{V}_{12} \\ \hat{V}_{21} & \hat{H}_{22} + \delta\omega \hat{I} \end{pmatrix} \begin{pmatrix} \hat{R}_1 & 0 \\ 0 & \hat{R}_2 \end{pmatrix} \\ &= \begin{pmatrix} \hat{H}^{(1)} & \hat{R}_1^{-1} \hat{V}_{12} \hat{R}_2 \\ \hat{R}_2^{-1} \hat{H}_{21} \hat{R}_1 & \hat{H}^{(2)} + \delta\omega \hat{I} \end{pmatrix}. \end{aligned} \quad (7)$$

In this representation each sub-system Hamiltonian  $\hat{H}^{(n)}$  is diagonal. Neglecting the coupling between sub-systems,  $\hat{H}_{12}^{QA} = \hat{R}_1^{-1} \hat{V}_{12} \hat{R}_2 \approx 0$ , and using a counter-intuitive sequence of pulses, the Hamiltonian has two parallel (independent) dark states as in STIRAP. Therefore, the differences between APLIP and STIRAP must come from the inter sub-system couplings. Substituting  $\cos(\theta_n) = \Omega_{nn}^{(2)}/\Omega_{nn}^{(e)}$  and  $\sin(\theta_n) = \Omega_{nn}^{(1)}/\Omega_{nn}^{(e)}$  where  $\Omega_{nn}^{(e)} = \left( (\Omega_{nn}^{(1)})^2 + (\Omega_{nn}^{(2)})^2 \right)^{\frac{1}{2}}$ , we obtain, for our reduced 6-level Hamiltonian:

$$\hat{H}_{12}^{QA} = (\hat{H}_{21}^{QA})^\dagger = \begin{pmatrix} \frac{\sin \varphi_1 \cos \varphi_2}{\Omega_{11}^{(e)}} (\Omega_{11}^{(1)} \Omega_{12}^{(1)} + \Omega_{11}^{(2)} \Omega_{12}^{(2)}) & -\frac{\cos \varphi_1}{\Omega_{22}^{(e)}} (\Omega_{22}^{(1)} \Omega_{12}^{(2)} - \Omega_{22}^{(2)} \Omega_{12}^{(1)}) & -\frac{\sin \varphi_1 \sin \varphi_2}{\Omega_{11}^{(e)}} (\Omega_{11}^{(1)} \Omega_{12}^{(1)} + \Omega_{11}^{(2)} \Omega_{12}^{(2)}) \\ +\frac{\cos \varphi_1 \sin \varphi_2}{\Omega_{22}^{(e)}} (\Omega_{22}^{(1)} \Omega_{12}^{(1)} + \Omega_{22}^{(2)} \Omega_{12}^{(2)}) & & +\frac{\cos \varphi_1 \cos \varphi_2}{\Omega_{22}^{(e)}} (\Omega_{22}^{(1)} \Omega_{12}^{(1)} - \Omega_{22}^{(2)} \Omega_{12}^{(2)}) \\ -\frac{\cos \varphi_2}{\Omega_{11}^{(e)}} (\Omega_{11}^{(1)} \Omega_{12}^{(2)} - \Omega_{11}^{(2)} \Omega_{12}^{(1)}) & 0 & \frac{\sin \varphi_2}{\Omega_{11}^{(e)}} (\Omega_{11}^{(1)} \Omega_{12}^{(2)} - \Omega_{11}^{(2)} \Omega_{12}^{(1)}) \\ \frac{\cos \varphi_1 \cos \varphi_2}{\Omega_{11}^{(e)}} (\Omega_{11}^{(1)} \Omega_{12}^{(1)} + \Omega_{11}^{(2)} \Omega_{12}^{(2)}) & \frac{\sin \varphi_2}{\Omega_{22}^{(e)}} (\Omega_{22}^{(1)} \Omega_{12}^{(1)} - \Omega_{22}^{(2)} \Omega_{12}^{(1)}) & -\frac{\cos \varphi_1 \sin \varphi_2}{\Omega_{11}^{(e)}} (\Omega_{11}^{(1)} \Omega_{12}^{(1)} + \Omega_{11}^{(2)} \Omega_{12}^{(2)}) \\ -\frac{\sin \varphi_1 \sin \varphi_2}{\Omega_{22}^{(e)}} (\Omega_{22}^{(1)} \Omega_{12}^{(1)} + \Omega_{22}^{(2)} \Omega_{12}^{(2)}) & & -\frac{\sin \varphi_1 \cos \varphi_2}{\Omega_{22}^{(e)}} (\Omega_{22}^{(1)} \Omega_{12}^{(1)} + \Omega_{22}^{(2)} \Omega_{12}^{(2)}) \end{pmatrix}. \quad (8)$$

Now let us concentrate in the case when both Rabi frequencies are equal,  $\mu_{12}A_1 = \mu_{23}A_2 = \Omega_0$ . We consider the initial state to be the ground vibrational level,  $|\phi_0^{(1)}\rangle$

which initially correlates with  $|\Phi_0^{(1)}\rangle$ . Then the only non zero couplings between this state and any other quasi-adiabatic state are

$$\langle \Phi_+^{(2)} | H_{21}^{QA} | \Phi_0^{(1)} \rangle = -\cos \varphi_2 (p_{11}^{12} p_{21}^{23} - p_{21}^{12} p_{11}^{23}) \frac{\Omega_0 S_1(t) S_2(t)}{\sqrt{(\Omega_{11}^{(1)}(t))^2 + (\Omega_{11}^{(2)}(t))^2}}, \quad (9)$$

and

$$\langle \Phi_-^{(2)} | H_{21}^{QA} | \Phi_0^{(1)} \rangle = \sin \varphi_2 (p_{11}^{12} p_{21}^{23} - p_{21}^{12} p_{11}^{23}) \frac{\Omega_0 S_1(t) S_2(t)}{\sqrt{(\Omega_{11}^{(1)}(t))^2 + (\Omega_{11}^{(2)}(t))^2}}. \quad (10)$$

Equations (9), and (10) separate the molecular contribution (geometrical factors) from the pulse contribution (depending on the pulse amplitude). However it can be seen that the APLIP dynamic behavior cannot stem from these terms. For instance, in the model of symmetrically displaced harmonic oscillators the symmetry of the system imposes that  $p_{12}^{12} = p_{21}^{23}$  and  $p_{11}^{23} = p_{11}^{12}$ . Therefore the quasi-adiabatic initially populated state,  $|\Phi_0^{(1)}\rangle$ , is not coupled with the rest of the system. So, this state

is indeed the adiabatic state whose evolution reproduces exactly the STIRAP behavior independently from the detuning or intensity of the pulses.

Increasing the number of vibrational levels in the expansion (Eq. (2)) does not introduce any different type of couplings and the same conclusions apply. It is very simple to generalize the expression for the general  $3N$ -level system, in this case, the Hamiltonian matrix terms are:

$$\begin{aligned} \langle \Phi_0^{(n)} | H^{QA} | \Phi_0^{(m)} \rangle &= 0 \\ \langle \Phi_0^{(n)} | H^{QA} | \Phi_+^{(m)} \rangle &= -\Omega_0 \cos \varphi_m (p_{nn}^{12} p_{nm}^{23} - p_{nm}^{12} p_{nn}^{23}) \frac{S_1(t) S_2(t)}{\sqrt{(p_{nn}^{12} S_1(t))^2 + (p_{nn}^{23} S_2(t))^2}} \\ \langle \Phi_0^{(n)} | H^{QA} | \Phi_-^{(m)} \rangle &= \Omega_0 \sin \varphi_m (p_{nn}^{12} p_{nm}^{23} - p_{nm}^{12} p_{nn}^{23}) \frac{S_1(t) S_2(t)}{\sqrt{(p_{nn}^{12} S_1(t))^2 + (p_{nn}^{23} S_2(t))^2}}. \end{aligned} \quad (11)$$

For the SDHO model, the geometrical symmetry requires that:  $p_{11}^{12} = \langle \phi_1^{(1)} | \phi_1^{(2)} \rangle = \langle \phi_1^{(2)} | \phi_1^{(3)} \rangle = p_{11}^{23}$ , and  $p_{12}^{12} = \langle \phi_1^{(1)} | \phi_2^{(2)} \rangle = \langle \phi_2^{(2)} | \phi_1^{(3)} \rangle = p_{21}^{23}$ . Once again, this makes any couplings involving the  $|\Phi_0^{(n)}\rangle$  states identi-

cally zero. The system exhibits  $N$  parallel (independent) trapped states. Therefore, if the initial wave function is a coherent superposition of vibrational levels of the ground electronic state,  $|\Psi(x, 0)\rangle = \sum_{n=0}^N a_n(0) |\phi_n^{(1)}(x)\rangle$ , a sequence of two coherent counter-intuitive pulses

will read this wave function in the adiabatic representation as  $|\Psi(x, 0)\rangle = \sum_{n=0}^N a_n(0) |\Phi_0^{(n)}(x, 0)\rangle$ , that will adiabatically passage at final times to  $|\Psi(x, T)\rangle = \sum_{n=0}^N a_n(0) \exp(-i(n-1)\delta\omega T) |\phi_n^{(3)}(x)\rangle$  (where the phase factor only depends on the eigenvalues of the dressed states  $|\Phi_0^{(n)}\rangle$ , i.e. the geometrical or Berry phase is zero). At each instant of time only the initial levels  $|\phi_n^{(1)}\rangle$  and the corresponding  $|\phi_n^{(3)}\rangle$  levels are populated, the final population in  $|\phi_n^{(3)}\rangle$  being completely determined by the initial population,  $|a_n(0)|^2$ . The same conclusion applies for the final probabilities if the initial state is an incoherent sum of vibrational levels. The dynamics follows as  $N$  independent STIRAP type systems and does not reproduce the characteristic features of APLIP.

This result is in flagrant contradiction with the numerical evidence (direct solution of the TDSE with the Hamiltonian of Eq.(1)), in which many of high energy vibrational levels of the ground and final potentials are considerably populated (Fig. 1(b)). Although the ana-

lytic proof derived in this paper is valid for a specific “ideal” system, the SDHO model, of course any small asymmetry in the model cannot explain the clear difference in behavior of STIRAP and APLIP. The difference, therefore, must stem from a different source. The validity of the quasi-adiabatic Hamiltonian rests upon the adiabatic approximation, that is, the neglect of the contribution from all the terms coming from  $\hat{R}^{-1}\hat{R} = \hat{R}_1^{-1}\hat{R}_1 \oplus \hat{R}_2^{-1}\hat{R}_2 \oplus \dots \oplus \hat{R}_N^{-1}\hat{R}_N$ , that couple states  $\Phi_0^{(n)}$  and  $\Phi_{\pm}^{(n)}$  belonging to the same sub-system. In STIRAP, the adiabatic condition,  $\Omega_0\tau \gg 1$  guarantees that these terms can be neglected. Surprisingly enough, for very large  $\Omega_0$  and detuning, the APLIP dynamics shows that the contribution of these terms cannot be neglected. This is in agreement with the numerical results obtained for population transfer by shaping LIPs in more general scenarios [3, 6].

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